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Some electronic and magnetic properties of Fluoride ion in Fluoride structure nanocrystals

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ABSTRACT

We have investigated the effects of the environment potential around Fluoride ion on some important electronic and magnetic properties such as dipole polarisability, moment of oscillator strengths $S(k)$ and magnetic susceptibility. The theoretical procedure is based on the variational-perturbation theory with two parameter trial functions incorporated in an ionic model. We estimate these properties in four cases for Fluoride ion; free ion, ion under different potentials, ion in the crystals and ion in nanocrystal, CdF_2, CaF_2, PbF_2, SrF_2 and BaF_2. Our results indicate that these properties vary with ion environments and the free state of Fluoride ion has higher values and there is linearity behaviour of these properties with lattice constant. For Fluoride ion in nanocrystal, we have found that there is an extra parameter that can also affect the dipole polarisability, the number of ions in the structure.

1. Introduction

Many important atomic properties such as dipole polarisability, total inelastic scattering cross section and stopping power are dependant on the moments of dipole oscillator strength distribution. It is related to many optical phenomena dispersion of atoms, assessing the quality of ab initio wave function and also plays a dominant role in the theory of intermolecular interactions [1–3]. Also the relationship between dipole polarisability and dielectric constant or refractive index which they hold by Clausius–Mosotti relation [4] makes these properties very important. Many studies focused on the electronic polarisability for Fluoride ion in alkali halides crystals and on the moment of oscillator strength distribution of atoms [5–13]. An approach was proposed by Yatsenko [8] to calculate the electronic dipole polarisability of ions in crystals which is based on an analysis of the relationship between the electronic dipole polarisability of ion and its effective charge while Hohm et al. [9] proposed a new relationship connecting the dipole polarisability, radius and Ionisation potential of atoms to calculate the atomic dipole polarisability of the 101 elements from He to No. Also the relativistic couple-cluster of dipole polarisability in closed shell atoms was investigated with the effects of electron correlation at the ground states of the alkaline earth metals [10].

Crystals with Fluoride structure such as BaF_2, CaF_2 and LiF are used to manufacture windows, prisms and lenses to be operated over the whole spectral range from UV and visible to the near and middle IR. Barium Fluoride (BaF_2) is relatively hard but it is extremely sensitive to thermal shock. For its transmittance 1–11 μm, the material is used for optical windows, lenses and prisms in UV-IR range. It is commonly used as a scintillated material for Gamma ray and fastest scintillating crystals [8]. Also it is used in the correction paret of the lens system, radiation resistant and it is susceptible to laser damage threshold [14]. Calcium Fluoride (CaF_2) is an ionic crystal insulator. The usefulness of its application lies in UV as Eximer laser windows. Many basic growth and analysis techniques such as Molecular Beam Epitax (MBE) and X-ray Photo Spectroscopy (XPS) are used to grow CaF_2 films on Si (1 1 1). Pure CaF_2 crystal has excellent transmission properties without absorption bands over a wide wave length range from UV to IR [15]. Selective absorption band exists in CaF_2 if the crystal contains impurities. Lithium Fluoride (LiF) shows an excellent transmittance in the VUV region. It is used for windows, prisms in the visible and infrared in 0.104–7 μm region and also it is sensitive to thermal shock. There are measurements of the intrinsic birefringence in CaF_2 and BaF_2 for wave length in the range of 365–156 nm [16].

2. Mathematical procedure

2.1. Dipole polarisability

Assume an external static electric field F along the normal to a given system (z-direction) acting on the atom or ion; the resulting energy shifts in second order due to F are given by $-\alpha F$, where α is

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the dipole polarisability of a given atom or ion. The energy shift can be estimated variationally. The trial function Φ is taken in the following form:

$$\phi = \phi_o(1+\omega) \tag{1}$$

where Φ_o is an unperturbed wave function and w is a symmetric function:

$$\omega = U(r_i) \tag{2}$$

The trial function $U(r_i)$ should contain the necessary parameters β_i and one of its appropriate form is the following [17,18]:

$$U(r) = F_z(\beta_i, r)H \tag{3}$$

where β_i are the two variational parameters and $H^{'}$ is the perturbed field which takes the Legendre polynomial of order L. In our recently work, we generalised this method for multipole polarisability [19]. For dipole $L = 1$ and the values of β_i can be derived to give minimum energy and then the dipole polarisability is given:

$$\alpha = -\sum_{i=1}^{2}\left(\frac{3}{4}\left(A_i\sum_{j=1\,j\neq i}^{2}\beta_i\beta_j + B_i\beta_i + iA_{2i}\beta_i^2\right)\right. \tag{4}$$

where

$$A_k = \langle\phi_o|r_i^{k-2}|\phi_o\rangle \quad \text{and} \quad B_k = \langle\phi_o|r_i^{k-1}(r_i\cdot r_j)|\phi_o\rangle \tag{5}$$

and Φ_o is approximated by a single Slater determinate.

A_k contributions involve the sum of terms each of which is associated with a single one-electron orbital ($i = j$) while B_k contains both diagonal and non diagonal terms ($i \neq j$) expressing the coupling between two one-electron states of different angular momenta.

2.2. Crystalline environment

The variation-perturbation approach was extended to consider F^- ion in various spherical hollow sphere potential V_o to corresponding bulk configuration using available orbitals [20]. This potential has been varied from 0.523 to 0.675 a.u. to demonstrate the electrostatic properties' dependence on the environment binding. The actual Madelung potential for these Fluoride structure crystals in this study lies approximately within the range of V_o. In a given potential V_o, any of those electronic properties can be approximately expressed as:

A third order polynomial has been obtained with the parameters D_i that are calculated from the values of V_o. The Madelung potential for any crystal V_m is given by:

$$V_m = \frac{Ze^2M}{4\pi\varepsilon_o d} \tag{6}$$

where d is the nearest neighbour distance and M is the Madelung constant for these Fluoride structure crystals. Here in this study, we assume that the CdF_2 and other structures are characterised by 100% ionic bonding.

2.3. Moment of oscillator strength

Moment of oscillator strength sum S(k) is defined in terms of spherical average oscillator strength f_{no} and corresponding transition energy E by the following relation:

$$S(k) = \sum_n f_{no}E_{no}^k \tag{7}$$

where the summation above is run over all the discrete and continuous states. By substituting (H–E_o) for E and the commutation relationship $[H,X_i] = -I\ P_{xi}(X_i = z,y,z)$, the well known sum rules are obtained[20.21]:

$$S(-1) = \frac{2}{3}\left[\left\langle\phi_o\middle|\sum r_i\middle|\phi_o\right\rangle + \left\langle\phi_o\middle|\sum r_i\cdot r_j\middle|\phi_o\right\rangle\right] \tag{8}$$

Eq. (8) involves one and two electron parts: The first term is directly related to the diamagnetic susceptibility χ as:

$$\chi = -\left(\frac{e^2}{6mc^2}\right)\left\langle\phi_o\middle|\sum r_i^2\middle|\phi_o\right\rangle \tag{9}$$

where e is the electron charge, m is the mass of electron and c is the light velocity. In terms of the second order distortion; the sum of the dipole oscillator strength is given [21,22]:

$$S(-2) = \frac{1}{8}\left[\sum_{k=1}^{3}g\left\langle\phi_o\middle|\sum r_i^{k-1}\middle|\phi_o\right\rangle\beta_1^{3-k}\beta_2^{k-1} + 2.333\left\langle\psi_o\middle|\sum r_i\middle|\phi_o\right\rangle\beta_1^n\beta_2^n\right] \tag{10}$$

where $g = k + 1$ and $n = 1$.

2.4. Nanocrystals

Madelung factor can be calculated from the following relation [19]:

$$M_f(i) = -\sum_{j=1,i\neq j}^{n} c(i)c(j)/r(ij) \tag{11}$$

where $M_f(i)$ is the Madelung factor for an individual ion. $C(i)$ is the charge of this ion, $c(j)$ is the charge on the surrounding ions, $r(ij)$ is their interionic distance and n the total number of ions in the nanoparticle. For an infinite array in which all ions can be considered to be in identical environments ($n = \infty$ in Eq. (11)), there is only one Madelung factor; a constant value. In real materials ($n \neq \infty$), there is a range of Madelung factor corresponding to ions in different environments rather than of a single value of Madelung factor. The final step is to calculate each ion's Coulombic interactions with all surrounding ions and to sum the results. From Eq. (6), Madelung potential also varies with Madelung factor(i.e., the number of ions) in nanocrystal while in the crystal it has a constant value.

3. Results

Table 1 shows $S(-2)$, $S(-1)$, α and χ for F^- ion with different potentials created by a hollow sphere around F^- ion, F^- ion embedded in the sphere with a opposite charge. For free state, $S(-2)$, $S(-1)$, α and χ for F^- ion has higher values and when comparing with bound states, the potential around the ion increases. These properties vary when the environment around the ion is changed, such as a crystalline environment. The data in this table can be used with Eq. (6), to estimate the three parameters $D_i(i = 1,2,3.)$ of the third degree polynomial. Then the values of D_i can be used with Madelung potential (Eq. (7)) to calculate α and $S(-2)$ for F^- ion in crystalline environment.

In Table 2, we have presented our calculations of Madelung potential and dipole polarisability and moment of dipole oscillator strength for the Fluoride ion in Fluoride crystals with infinite

Table 1
Moment of oscillator strength $S(-2)$, $S(-1)$ and $S(0)$, dipole polarisability α (10^{-3} nm^3) and magnetic susceptibility $\chi(-10^{-6}$ cm/mol) of F^- ion in the different hollow sphere potential V(a.u.).

Ion	V	$S(-2)$	$S(-1)$	$S(0)$	α	χ
F^-	free	4.558	7.45	9.99	2.702	12.62
	0.52	3.190	6.13	9.99	1.895	10.99
	0.57	3.151	6.09	10.0	1.868	10.89
	0.67	3.117	6.00	9.99	1.848	10.82

Table 2
Madelung potential (a.u), dipole polarisability $\alpha(10^{-3}\,nm^3)$ and moment of dipole oscillator strength $S(-2)$ of F^- ion in some compounds of Fluoride structure crystals.

Crystal	V_m	α	α [17]	$S(-2)$
CdF_2	0.679	1.764		2.975
CaF_2	0.669	1.811	2.45	3.055
pbF_2	0.617	1.980		3.340
BaF_2	0.590	2.155	3.76	3.635
SrF_2	0.538	2.37	2.98	3.998

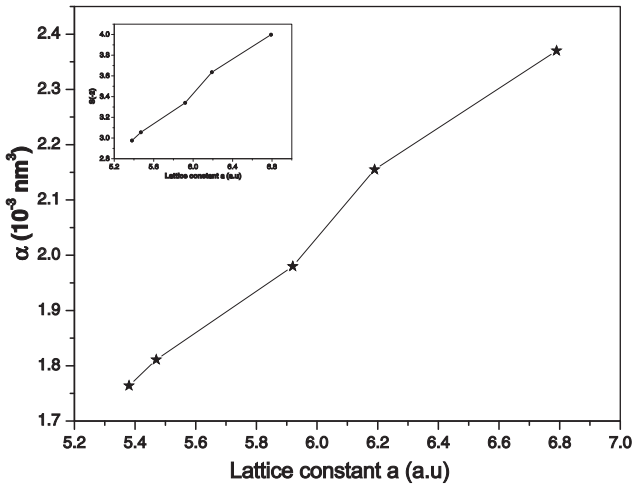

Fig. 1. Dipole polarisability and dipole oscillator strength $S(-2)$ versus lattice constant a for CdF_2, CaF_2, pbF_2, BaF_2 and SrF_2. The linearity behaviour of these properties with lattice constant is very clear.

number of ions(i.e., Madelung constant equal to 1.7476). α and $S(-2)$ of F^- ion are affected by the environment around the ion. They vary with Madelung potential which depends on the nearest neighbour distance, lattice constant. As Madelung potential increases α and $S(-2)$ of F^- ion decrease. From Eq. (4), there are four terms: the first term is constant then the dipole polarisability proportional with the inverse of the lattice constant. This means that it is the dominant part for the dipole polarisability. In Fig. 1, we have plotted the variation of α and $S(-2)$ as a function of the effective crystal potential for CdF_2, CaF_2, PbF_2, BaF_2 and SrF_2 crystals with Fluoride structure. We observe that there is linearity behaviour of these parameters with potential and increasing the potential around the ion causes the dipole polarisability and dipole oscillator strength to decrease. The effective potential depends only on the lattice constant in the crystals with an infinite number of ions. We also estimate $S(0)$ which represents the number of the electrons in the Fluoride ion to check our calculations. Our results for dipole polarisability of F^- ion in Fluoride structure crystals approximately agree with the results obtained by using local density approximation and under the point charge approximation [23]. Maximum value of α was found equal to 1.09 10^{-3} nm^3 [18] and in another study, it was found ranging from 0.75×10^{-3} to 2.95×10^{-3} nm^3 [24]. α_{Sr} and α_F in SrF_2 are found to be 1.186×10^{-3} and 0.975×10^{-3} nm^3, respectively and α_{Ba} and α_F in BaF_2 are found to be 2.088×10^{-3} and 0.974×10^{-3} nm^3 respectively [25]. Different results with different methods are obtained in other studies. α_{Sr} and α_F in SrF_2 are found to be 0.75×10^{-3} and 1.129×10^{-3} nm^3, respectively, and α_{Ba} and α_F in BaF_2 are found to be 1.54×10^{-3} and 1.198×10^{-3} nm^3 respectively [24].

For nanocrystal, the effective potential (i.e., Eq. (6)) depends on two parameters, lattice constant and Madelung factor. Madelung factor depends on the number of ions in the structure. For Fluoride

Table 3
Number of atoms and dipole polarisability $\alpha(10^{-3}\,nm^3)$ for F^- ion in five Compounds of Fluoride structure nanocrystals.

No. of atoms	α				
	CdF_2	CaF_2	PbF_2	BaF_2	SrF_2
27	1.762	1.885	1.990	2.288	2.360
216	1.761	1.882	1.987	2.282	2.354
729	1.758	1.875	1.976	2.264	2.334
3375	1.753	1.860	1.955	2.228	2.295
27000	1.746	1.840	1.927	2.180	2.242
216000	1.740	1.817	1.892	2.119	2.175
729000	1.733	1.752	1.790	1.923	1.960

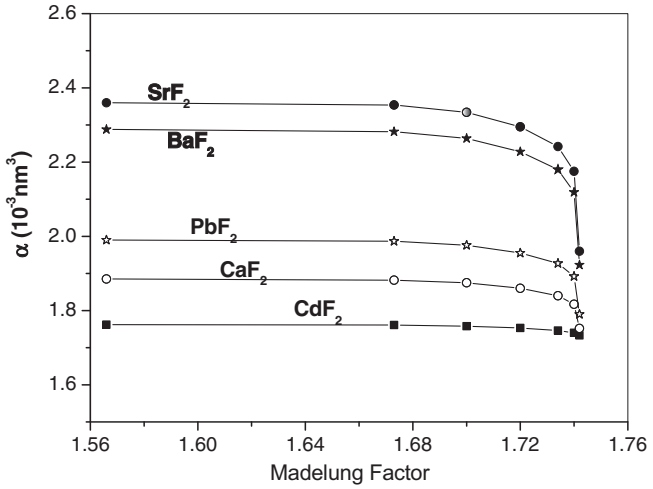

Fig. 2. Dipole polarisability as a function of Madelung factor for Fluoride ion in CdF_2, CaF_2, pbF_2, BaF_2 and SrF_2 nanocrystals. As the number of ions increases in the crystal the potential around the ion will increase and then α decreases.

crystals adopted here in this study, there is odd number of ion in nanocrystals. Two Fluoride ions and one positive ion with two electrons valence such as Cd^{+2},Ca^{+2}, Pb^{+2}, Ba^{+2} and Sr^{+2}. In Table 3, we present our calculations of the number of ions in five compounds of Fluoride structure nanocrystals (i.e., equiv. to Madelung factor) and dipole polarisability. Fig. 2 shows the effects of the number of ions on the dipole polarisability. We observe that as the number of ions increases in the crystal the effective potential around the ion will also increase and this will cause to reduce the value of the dipole polarisability of the ion.

Our model is an ionic model (i.e., well potential), so it is very suitable with pure crystals. The crystals CdF_2 and PbF_2 are covalent crystals and they have some percentage of iconicity cause to appear the polarisability and for this reason we expect less accuracy in the calculations for these compounds. For more accuracy, we must calculate the molecular orbitals instead of atomic orbitals. This will lead to more difficulties and heavy burden and in this model we plan to win time, cost and more simplicity.

4. Conclusion

Ionic model and a variational-perturbation scheme with two parameter trial functions give us suitable results for calculating the electronic and magnetic properties of the free ion and ion in the crystal structure. Electronic dipole polarisability, oscillator strength sum and magnetic susceptibility of ion are very sensitive to their environment. As the effective potential around F^- ion decreases the electronic polarisability and dipole oscillator strength increase, they vary with lattice constant as linearity behaviour in

crystal with infinite number of ions in the crystal. In nanocrystal, we found that the number of ions has an effect on the dipole polarisability as we added more ions to the structure and this will cause to increase the potential around the ion and then reduce the value of dipole polarisability of the ion. Also, our ionic model which was adopted in this study is very simple and gives reasonably good results. We hope that our results of dipole polarisability, dipole oscillator strength and magnetic susceptibility will be useful data for other studies especially for nanocrystal.

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